STEALING IDEAS FROM ELECTRONIC STRUCTURE THEORY TO IMPROVE VIBRATIONAL CALCULATIONS. PART II - THE WAVEFUNCTION

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The fields of electronic and vibrational structure theory have largely evolved independently over the years. Demonstrative of this is the fact that the electronic-structure community has generally embraced coupled-cluster wavefunctions as the gold standard for small, well-behaved systems, while vibrational structure practitioners tend to prefer treatments based on vibrational perturbation theory or configuration interactions. While this is not surprising — the two fields face dramatically difference challenges and goals — one does wonder if ideas from one can be used to improve or inform the other.

To this point, Part II of this presentation borrows the diagrammatic techniques of electronic coupled-cluster to develop a set of Davidson-like corrections to the vibrational CI wavefunction, which help resolve some of the size-consistency problems that can arise in VCI calculations. The goal is to present these (somewhat complicated) concepts in a way accessible to theorists from both fields, as well as to the broader field of spectroscopists as a whole.